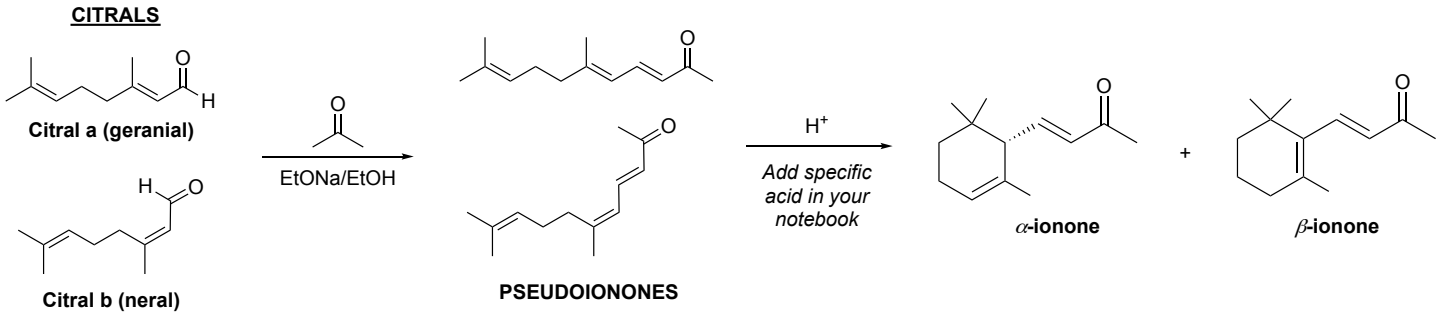
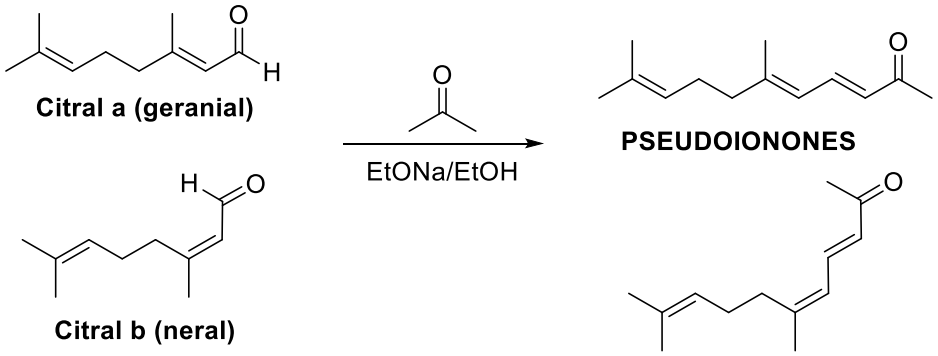
CHEM 110L, Experiment 2 – Two-Step Synthesis of Ionones



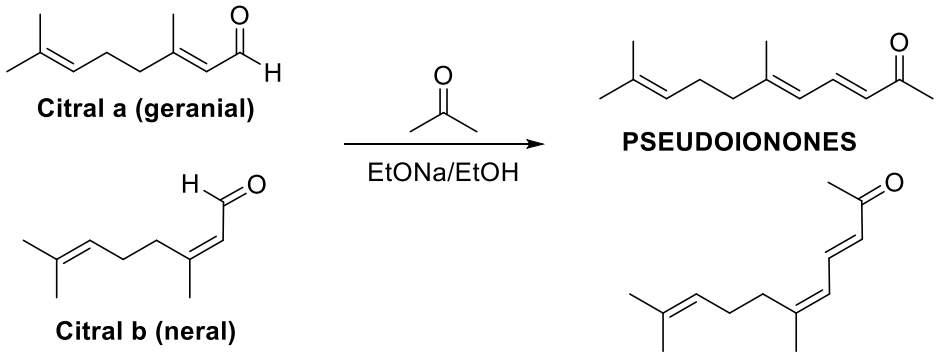
Part A – Pseudoionone Synthesis – Aldol Condensation with Dehydration

Reaction Setup

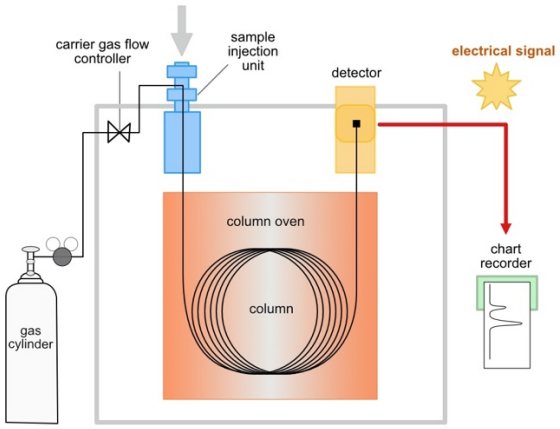


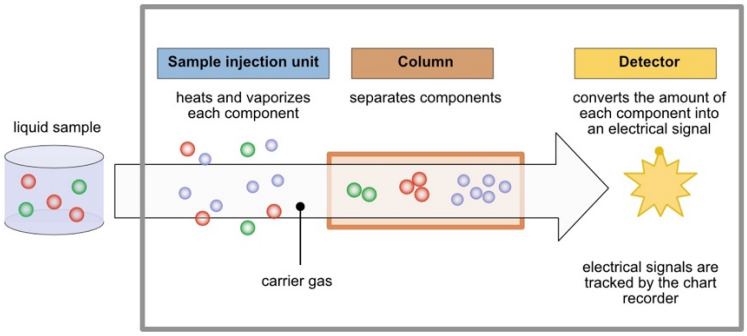
Reaction Workup: (1) HCl **(2)** 15 mL BME **(3)** H_2O **(4)** 2 x 5 mL BME **(5)** NaCl **(6)** $MgSO_4$

Part A Analysis: % yield, IR, GC, ^{1}H NMR



Gas Chromatography (GC) Refresher

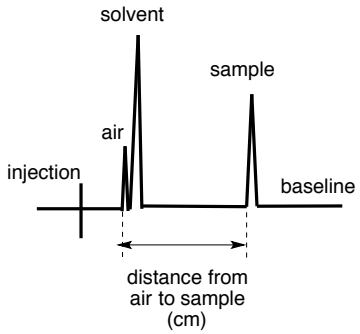




Corrected Retention Time (t_R')

Peak Integration and Percent Composition

- Peak Identification



$$t_R' \text{ (sec)} = \text{distance from air to sample (cm)} \times \frac{\text{chart speed } 1 \text{ min}}{2.5 \text{ cm}} \times \frac{60 \text{ sec}}{1 \text{ min}}$$

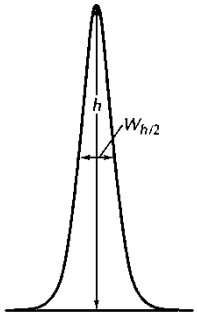


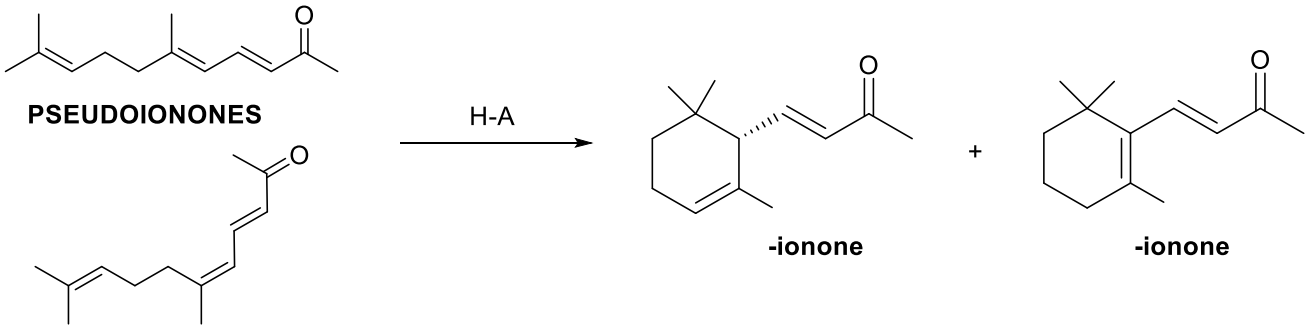
FIGURE 20.13
Determining peak area: h = height; $W_{h/2}$ = width at half-height.

Integration: Peak Area = h x $w_{h/2}$

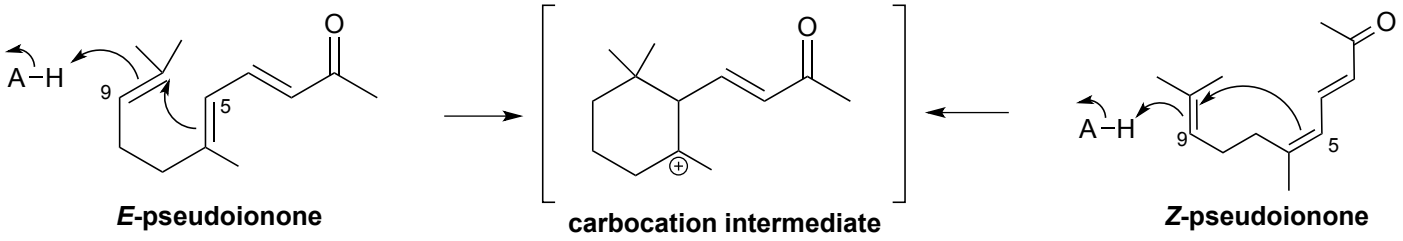
% Composition of A =

Part B – Ionone Synthesis: Acid-Catalyzed Cyclization of Pseudoionones

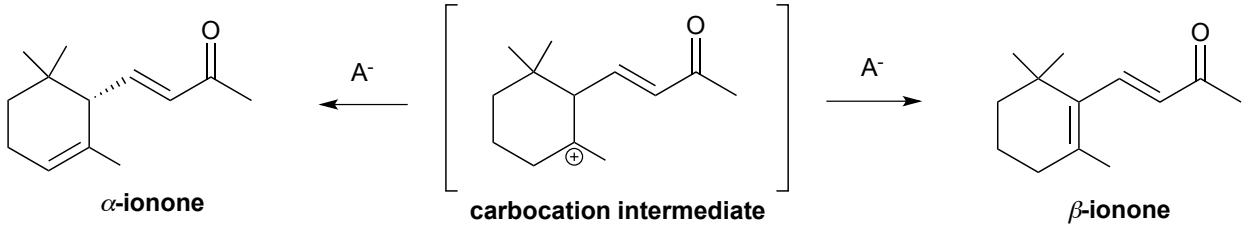
H-A options: $\underline{H_2SO_4 / HAc}$ or $\underline{H_3PO_4}$



Intramolecular Alkene Addition



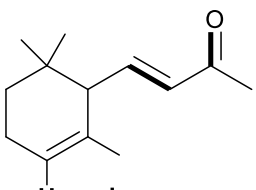
Alkene Formation (E1-Style)



Sulfuric / Acetic Acid Rxn Workup: Prepare a mixture of 30 mL of cold water and 6 mL of BME in a flask. Swirl, then transfer to the reaction mixture, mix, and transfer it to a separatory funnel. Extract the product into the organic layer. Separate the layers and extract the aqueous layer with an additional 6 mL of BME. Wash the combined organic layers with 2 x 12 mL of an aqueous solution containing $NaHCO_3$ (5% w/v) and NaCl (10% w/v).

Phosphoric Acid Rxn Workup: Add 30 mL of aqueous NaCl (10% w/v) and transfer the mixture into a separatory funnel. Wash the flask with 15 mL of BME and transfer the wash to the separatory funnel. Mix and separate the layers. Extract the aqueous layer again with 15 mL of BME. Wash the combined organic layers first with 15 mL of an aqueous solution containing $NaHCO_3$ (5% w/v) and NaCl (10% w/v), followed by 15 mL of aqueous NaCl.

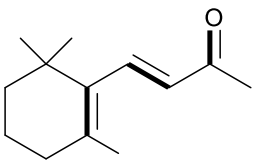
IR & UV-vis Spectroscopy of Products



H -ionone

Conjugated system with **2** orbitals

Additional vinylic C-H bend: IR 600-900cm^{-1}



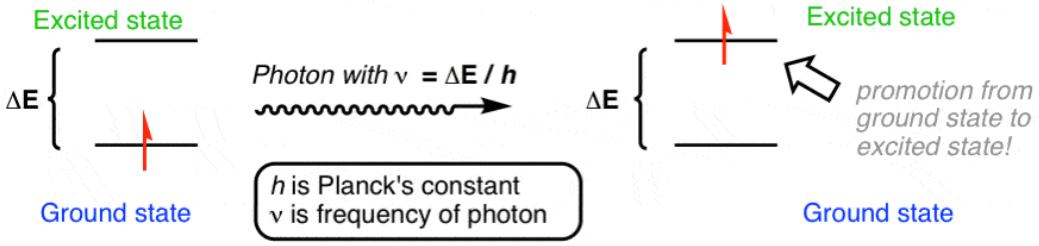
-ionone

Conjugated system with **3** orbitals

Strong UV absorbance at 295nm

Summary: UV -Visible Spectroscopy

- Absorption of a photon with frequency ν can cause a transition between a ground state and excited state separated by energy ΔE



Since E = *h*ν , absorption will occur when photon has frequency ν = **ΔE / *h***

or since c = ν λ , wavelength $\lambda = \frac{h\,c}{\Delta E}$

(c is speed of light)

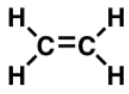
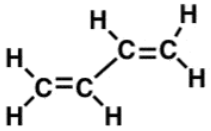
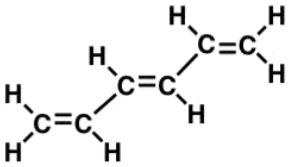
- In molecules with pi (π) bonds, the energy gap ΔE between electrons in the ground state (π) and excited state (π*) corresponds to photons in the ultraviolet (UV) and visible part of the electromagnetic spectrum (180 – 700 nm wavelength, or E = 40 - 160 kcal/mol)

- **Key Point:** As the number of conjugated (consecutive) π bonds increases, the energy gap (ΔE) decreases, meaning that light of less energy (longer wavelength) is absorbed.

- A **UV-Visible Spectrometer** lets us measure absorbance versus wavelength.

- The wavelength of maximum absorbance λ_{max} corresponds to ΔE

- **Therefore λ_{max} will be in the UV part of the spectrum for molecules with fewer conjugated π bonds and more toward the visible for molecules with many conjugated π bonds.**

Ethene ("**ethylene**")	Butadiene ("**1,3 butadiene**")	Hexatriene ("**1,3,5 hexatriene**")
		
1 pi bond	**2 conjugated pi bonds**	**3 conjugated pi bonds**
λ_{max} **180 nm (UV)**	λ_{max} **217 nm (UV)**	λ_{max} **258 nm (UV)**

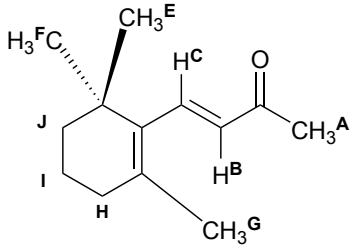
Fewer conjugated π bonds → lower λ_{max} (i.e. towards the UV)

More conjugated π bonds → higher λ_{max} (i.e. towards the visible)

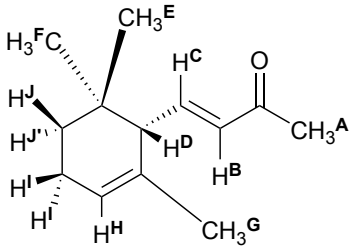
Therefore using UV-Vis spectroscopy to determine the λ_{max} of an unknown molecule can tell us about the π bonding present (if any)

https://www.masterorganicchemistry.com/2016/09/16/introduction-to-uv-vis-spectroscopy/

Describe each ^{1}H NMR term. Give a few examples, if any, from *alpha*- and/or *beta*-ionone.



β-ionone



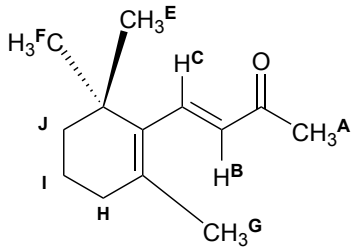
α-ionone

1. Heterotopic protons

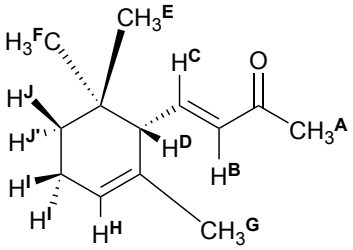
2. Equivalent protons (homotopic or enantiotopic)

3. Diastereotopic protons

Ionone Splitting Patterns & Assignments



β-**ionone**



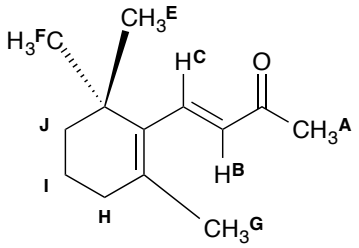
α-**ionone**

(a) What does is mean when a signal appears as a **singlet (s)**? Identify (chemical shift, ppm) and assign each **singlet in the ionone spectra** to a letter on the structures above to the best of your ability.

(b) What does is mean when a signal appears as a **doublet (d)**? Identify and assign each **doublet**.

(c) What does is mean when a signal appears as a **doublet of doublets (dd)**? Identify the **dd** in the spectrum (ppm) and assign it to the structure.

(d) What does is mean when a signal appears as a **triplet of triplets (tt)**? Identify (ppm) and assign any **tt**'s.



^{1}H NMR Analysis of β-ionone **β-ionone**

Signal	Integration (#H's)	Splitting (exp/obs)	Chemical Shift, Expected	Chemical Shift, Observed (Fig 20.3)
A	3			
B	1			
C	1			
D	-- N/A --			
E	3			
F	3			
G	3			
H	2			
I	2			
J	2			

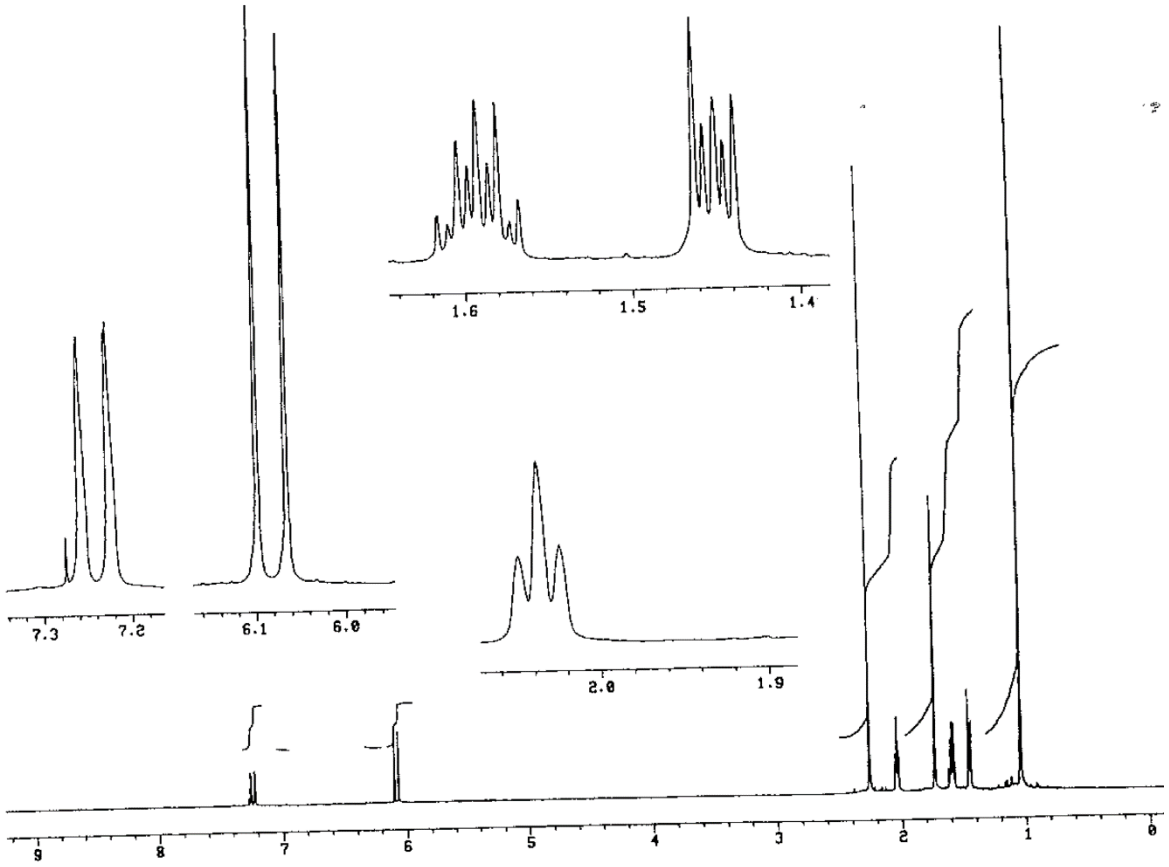
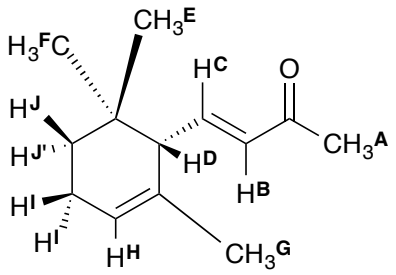


Figure 23.15 500-MHz ^{1}H-NMR spectrum of β-ionone in $CDCl_3$.



^{1}H NMR Analysis of α-ionone **α-ionone**

Signal	Integration (#H's)	Splitting (exp/obs)	Chemical Shift, Expected	Chemical Shift, Observed (Fig 20.3)
A	3			
B	1			
C	1			
D	1			
E	3			
F	3			
G	3			
H	1			
I	2			
J	1			
J'	1			

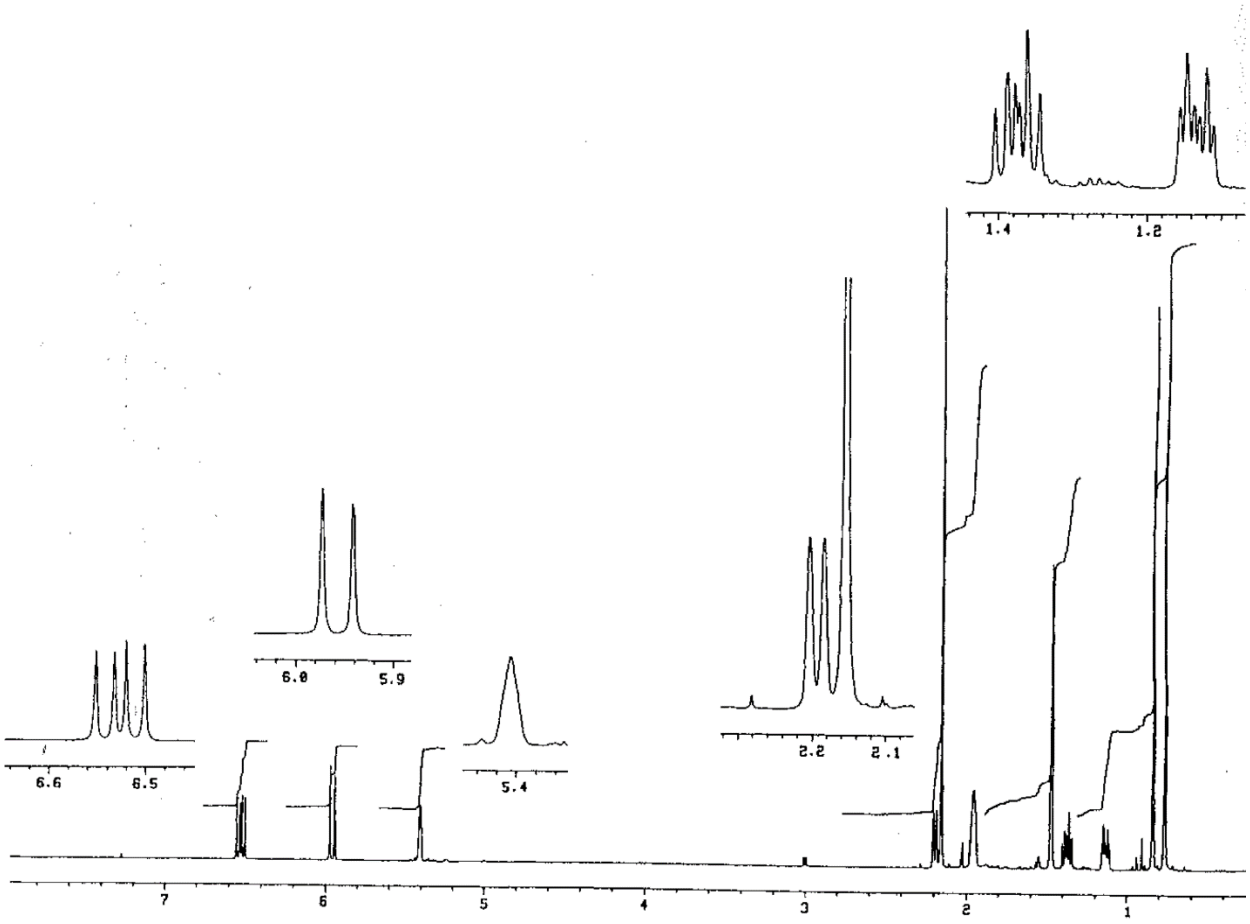


Figure 23.12 500-MHz ^{1}H-NMR spectrum of α-ionone in $CDCl_3$.